

Argonne National Laboratory

THE THERMODYNAMIC PROPERTIES OF
 P_2 , P_4 , AND SOME PHOSPHORUS FLUORIDES

by

P. A. G. O'Hare

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Chemical Engineering Division

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ABSTRACT

The thermodynamic functions S° , C_p° , $(H^\circ - H_0^\circ)/T$, $(G^\circ - H_0^\circ)/T$, and $(H^\circ - H_{298}^\circ)$ have been calculated for the ideal gas molecules P_2 , P_4 , PF , PF_2 , PF_3 , PF_4 , PF_5 , and P_2F_4 , by the formulas of statistical mechanics. In addition, the quantities ΔH_f , ΔG_f , and $\log K_f$, are also given; where experimental values were not available, estimates have been made. The thermodynamic data have been calculated at selected intervals between 0 and 6000°K, and also at 273.15 and 298.15°K. Some thermodynamic aspects of the reactions of phosphorus fluorides are discussed.

I. INTRODUCTION

This compilation, which forms part of a series,¹ deals with the ideal gas molecules P_2 , P_4 , PF , PF_2 , PF_3 , PF_4 , PF_5 , and P_2F_4 . Values for the thermodynamic functions S° , C_p° , $(H^\circ - H_0^\circ)/T$, $(G^\circ - H_0^\circ)/T$, $(H^\circ - H_{298}^\circ)$, ΔH_f , ΔG_f , and $\log K_f$ have been calculated and are tabulated at 273.15°K, at 298.15°K, and at selected intervals between 0 and 6000°K. In several instances, structural, spectral, and enthalpy-of-formation data had to be estimated.

Some thermodynamic aspects of the reactions of phosphorus fluorides are also discussed.

II. CALCULATIONS

The formulas used to calculate the thermodynamic functions, together with the values of the constants, have been given previously.^{1a} The atomic weights of phosphorus (30.9738) and of fluorine (18.9984) have been taken from the 1961 table of atomic weights.² Structural and spectral data used in the calculations are summarized in Table I.

TABLE I. Data Used in the Calculations

Compound	ω (cm ⁻¹)	M	ℓ (Å)	ϱ^a	I^b	σ	g_i	ΔH_f^C (kcal mol ⁻¹)
P								58.43 ± 0.1
P ₂	780.89 ($\omega_{\text{p}} \chi_{\text{p}} = 2.820$)	61.9476	1.8939		9.22360×10^{-39}	2	1	0.00
P ₄	606,464.5(3), 363(2)	123.8952	2.21	109° 28'	15825.6×10^{-117}	12	1	-54.9 ± 0.2
PF	846.75 ($\omega_{\text{p}} \chi_{\text{p}} = 4.489$)	49.9722	1.590		4.94310×10^{-39}	1	3	-26.3 ± 6.0
PF ₂	895, 776, 374	68.9706	1.537	104°	276.914×10^{-117}	2	2	-133 ± 5
PF ₃	892, 860(2), 487, 344(2)	87.9690	1.537	98° 12'	1838.37×10^{-117}	3	1	-246.65 ± 0.38
PF ₄	1025(2), 817, 778, 576, 533(2), 514(2)	106.9674	1.54	109° 28'	7941.80×10^{-117}	12	2	-322 ± 10
PF ₅	1025(2), 944.8, 817, 640 575.5, 534(2), 514(2), 300.6(2)	125.9658	1.534 (eq)	180° (ax) 60° (eq)	16025.2×10^{-117}	6	1	-398.05 ± 0.32
P ₂ F ₄	839, 828, 825, 803, 541, 453, 377, 365, 361, 214, 204, 150	137.9412	2.1 (P-P) 1.54 (P-F)	100° (FPF) 94° (FPFP)	96603.4×10^{-117}	2	1	-334 ± 15

^aInterbond angle.^bMoment of inertia for diatomic molecules (g cm²); product of moments of inertia for polyatomic molecules (g³ cm⁶).^cEnthalpy of formation with P₂(g) as reference state.

All enthalpy-of-formation values given in the tables in this report are referred to P₂(g) and F₂(g) as reference states.

Unless otherwise noted, thermochemical data given in this report refer to 298.15°K (25°C).

III. THERMODYNAMIC PROPERTIES

A. Diatomic Phosphorus, P₂(g)

Thermodynamic functions for P₂(g) have been reported by Stull and Sinke,³ Potter and DiStefano,⁴ and JANAF;^{5a} the data in Table II update previous compilations. The spectroscopic constants on which the present calculations have been based are taken from the work of Creutzberg.⁶

The enthalpy of formation of P₂(g) from α-white phosphorus was taken to be 34.5 kcal mol⁻¹.⁷

B. Tetra-atomic Phosphorus, P₄(g)

The thermodynamic properties for P₄(g) listed in Table III update those available from other sources.³⁻⁵ Spectroscopic and molecular data, summarized in Table I, are taken from the investigations by Gutowsky and Hoffman⁸ and Maxwell, Hendricks, and Moseley,⁹ respectively. Tetra-atomic phosphorus vapor has a tetrahedral structure.⁹

An experimental value for S°(P₄,g) can be deduced from the vapor pressure studies reported by Dainton and Kimberley.¹⁰ If P₄ vapor is

TABLE II. Thermodynamic Properties of Diatomic Phosphorus Gas

T (DEG.K.)	$-(G^{\circ}-H_0^{\circ})/T$ (GIBBS/MOL)	$(H^{\circ}-H_0^{\circ})/T$ (GIBBS/MOL)	S° (GIBBS/MOL)	C° P (GIBBS/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	37.318	6.9525	44.271	6.9586
200.00	42.145	6.9957	49.141	7.1907
273.15	44.339	7.0931	51.432	7.5327
298.15	44.962	7.1348	52.097	7.6475
300.00	45.006	7.1380	52.144	7.6557
400.00	47.084	7.3175	54.401	8.0342
500.00	48.735	7.4881	56.224	8.2888
600.00	50.114	7.6365	57.751	8.4567
700.00	51.301	7.7623	59.063	8.5702
800.00	52.345	7.8685	60.213	8.6494
900.00	53.277	7.9586	61.235	8.7063
1000.00	54.119	8.0356	62.155	8.7484
1100.00	54.888	8.1019	62.990	8.7804
1200.00	55.596	8.1595	63.755	8.8051
1300.00	56.251	8.2100	64.461	8.8247
1400.00	56.861	8.2544	65.116	8.8404
1500.00	57.432	8.2939	65.726	8.8532
1600.00	57.968	8.3292	66.298	8.8637
1700.00	58.474	8.3609	66.835	8.8725
1800.00	58.953	8.3896	67.343	8.8799
1900.00	59.407	8.4155	67.823	8.8861
2000.00	59.840	8.4392	68.279	8.8915
2200.00	60.646	8.4807	69.127	8.9002
2400.00	61.385	8.5160	69.901	8.9069
2600.00	62.068	8.5463	70.615	8.9120
2800.00	62.703	8.5725	71.275	8.9162
3000.00	63.295	8.5956	71.891	8.9195
3200.00	63.850	8.6159	72.466	8.9223
3400.00	64.373	8.6340	73.007	8.9245
3600.00	64.867	8.6502	73.517	8.9264
3800.00	65.335	8.6648	74.000	8.9280
4000.00	65.780	8.6780	74.458	8.9294
4200.00	66.204	8.6900	74.894	8.9306
4400.00	66.608	8.7009	75.309	8.9316
4600.00	66.995	8.7110	75.706	8.9325
4800.00	67.366	8.7202	76.086	8.9333
5000.00	67.722	8.7288	76.451	8.9340
5200.00	68.065	8.7367	76.802	8.9346
5400.00	68.395	8.7440	77.139	8.9352
5600.00	68.713	8.7509	77.464	8.9357
5800.00	69.020	8.7572	77.777	8.9361
6000.00	69.317	8.7632	78.080	8.9365

TABLE II (Contd.)

T (DEG.K.)	$(H^o - H_{298}^o)$ (KCAL/MOL)	- ΔH_f (KCAL/MOL)	- ΔG_f (KCAL/MOL)	LOG Kf
0.00	-2.1272	0.00	0.00	INF
100.00	-1.4320	0.00	0.00	0.00
200.00	-0.7281	0.00	0.00	0.00
273.15	-0.1898	0.00	0.00	0.00
298.15	0.0000	0.00	0.00	0.00
300.00	0.0142	0.00	0.00	0.00
400.00	0.7998	0.00	0.00	0.00
500.00	1.6168	0.00	0.00	0.00
600.00	2.4547	0.00	0.00	0.00
700.00	3.3064	0.00	0.00	0.00
800.00	4.1676	0.00	0.00	0.00
900.00	5.0355	0.00	0.00	0.00
1000.00	5.9083	0.00	0.00	0.00
1100.00	6.7848	0.00	0.00	0.00
1200.00	7.6642	0.00	0.00	0.00
1300.00	8.5457	0.00	0.00	0.00
1400.00	9.4290	0.00	0.00	0.00
1500.00	10.3137	0.00	0.00	0.00
1600.00	11.1995	0.00	0.00	0.00
1700.00	12.0864	0.00	0.00	0.00
1800.00	12.9740	0.00	0.00	0.00
1900.00	13.8623	0.00	0.00	0.00
2000.00	14.7512	0.00	0.00	0.00
2200.00	16.5304	0.00	0.00	0.00
2400.00	18.3111	0.00	0.00	0.00
2600.00	20.0931	0.00	0.00	0.00
2800.00	21.8759	0.00	0.00	0.00
3000.00	23.6595	0.00	0.00	0.00
3200.00	25.4437	0.00	0.00	0.00
3400.00	27.2283	0.00	0.00	0.00
3600.00	29.0134	0.00	0.00	0.00
3800.00	30.7989	0.00	0.00	0.00
4000.00	32.5846	0.00	0.00	0.00
4200.00	34.3707	0.00	0.00	0.00
4400.00	36.1569	0.00	0.00	0.00
4600.00	37.9433	0.00	0.00	0.00
4800.00	39.7299	0.00	0.00	0.00
5000.00	41.5166	0.00	0.00	0.00
5200.00	43.3035	0.00	0.00	0.00
5400.00	45.0905	0.00	0.00	0.00
5600.00	46.8776	0.00	0.00	0.00
5800.00	48.6648	0.00	0.00	0.00
6000.00	50.4520	0.00	0.00	0.00

TABLE III. Thermodynamic Properties of Tetra-atomic Phosphorus Gas

T (DEG.K.)	$-(C^o - H^o_0)/T$ (GIBBS/MOL)	$(H^o - H^o_0)/T$ (GIBBS/MOL)	S° (GIBBS/MOL)	C° P (GIBBS/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	45.371	8.1140	53.485	8.8984
200.00	51.395	9.6140	61.009	13.2934
273.15	54.588	10.9207	65.509	15.5131
298.15	55.562	11.3289	66.891	16.0509
300.00	55.632	11.3582	66.990	16.0871
400.00	59.098	12.7374	71.835	17.5093
500.00	62.057	13.7761	75.833	18.2803
600.00	64.642	14.5677	79.210	18.7344
700.00	66.936	15.1849	82.121	19.0213
800.00	68.997	15.6772	84.674	19.2130
900.00	70.867	16.0779	86.945	19.3471
1000.00	72.579	16.4099	88.989	19.4443
1100.00	74.156	16.6892	90.846	19.5170
1200.00	75.619	16.9273	92.546	19.5726
1300.00	76.982	17.1325	94.115	19.6162
1400.00	78.259	17.3112	95.570	19.6510
1500.00	79.458	17.4682	96.927	19.6791
1600.00	80.590	17.6071	98.197	19.7022
1700.00	81.661	17.7309	99.392	19.7214
1800.00	82.678	17.8420	100.520	19.7375
1900.00	83.646	17.9421	101.588	19.7512
2000.00	84.568	18.0329	102.601	19.7628
2200.00	86.295	18.1910	104.486	19.7816
2400.00	87.883	18.3242	106.207	19.7959
2600.00	89.355	18.4378	107.792	19.8071
2800.00	90.725	18.5360	109.261	19.8160
3000.00	92.006	18.6216	110.628	19.8231
3200.00	93.211	18.6968	111.908	19.8290
3400.00	94.346	18.7636	113.110	19.8339
3600.00	95.420	18.8232	114.244	19.8379
3800.00	96.440	18.8767	115.316	19.8414
4000.00	97.409	18.9250	116.334	19.8443
4200.00	98.334	18.9688	117.302	19.8469
4400.00	99.217	19.0088	118.226	19.8491
4600.00	100.063	19.0454	119.108	19.8510
4800.00	100.874	19.0790	119.953	19.8527
5000.00	101.654	19.1099	120.763	19.8542
5200.00	102.404	19.1386	121.542	19.8555
5400.00	103.126	19.1652	122.292	19.8567
5600.00	103.824	19.1899	123.014	19.8577
5800.00	104.498	19.2129	123.711	19.8587
6000.00	105.149	19.2345	124.384	19.8595

TABLE III (Contd.)

T (DEG.K.)	$(H^\circ - H^\circ_{298})$ (KCAL/MOL)	$-\Delta H_f$ (KCAL/MOL)	$-\Delta G_f$ (KCAL/MOL)	LOG Kf
0.00	-3.3777	54.04	54.04	INF
100.00	-2.5663	54.62	51.47	112.49
200.00	-1.4549	54.91	48.18	52.65
273.15	-0.3947	54.92	45.74	36.60
298.15	0.0000	54.90	44.87	32.89
300.00	0.0297	54.90	44.80	32.64
400.00	1.7172	54.77	41.46	22.65
500.00	3.5103	54.60	38.15	16.68
600.00	5.3629	54.42	34.88	12.70
700.00	7.2517	54.23	31.63	9.88
800.00	9.1640	54.04	28.42	7.76
900.00	11.0924	53.86	25.23	6.13
1000.00	13.0322	53.68	22.06	4.82
1100.00	14.9804	53.50	18.91	3.76
1200.00	16.9350	53.32	15.77	2.87
1300.00	18.8946	53.14	12.65	2.13
1400.00	20.8580	52.97	9.54	1.49
1500.00	22.8245	52.80	6.44	0.94
1600.00	24.7936	52.63	3.35	0.46
1700.00	26.7648	52.47	0.28	0.04
1800.00	28.7378	52.30	-2.78	-0.34
1900.00	30.7123	52.14	-5.84	-0.67
2000.00	32.6880	51.98	-8.89	-0.97
2200.00	36.6425	51.67	-14.96	-1.49
2400.00	40.6003	51.36	-21.00	-1.91
2600.00	44.5607	51.07	-27.02	-2.27
2800.00	48.5230	50.78	-33.02	-2.58
3000.00	52.4870	50.51	-38.99	-2.84
3200.00	56.4522	50.23	-44.95	-3.07
3400.00	60.4185	49.97	-50.89	-3.27
3600.00	64.3857	49.72	-56.82	-3.45
3800.00	68.3536	49.48	-62.73	-3.61
4000.00	72.3222	49.24	-68.63	-3.75
4200.00	76.2913	49.01	-74.52	-3.88
4400.00	80.2609	48.79	-80.40	-3.99
4600.00	84.2310	48.58	-86.26	-4.10
4800.00	88.2013	48.38	-92.12	-4.19
5000.00	92.1720	48.18	-97.97	-4.28
5200.00	96.1430	48.00	-103.82	-4.36
5400.00	100.1142	47.82	-109.65	-4.44
5600.00	104.0856	47.65	-115.48	-4.51
5800.00	108.0573	47.49	-121.30	-4.57
6000.00	112.0291	47.34	-127.12	-4.63

assumed to behave as a perfect gas, we may write

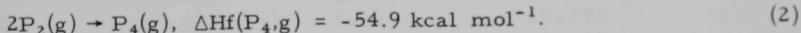
$$S^\circ(P_4, g)_{298} = 4S^\circ(P, \alpha\text{-white}) + \Delta H_v^\circ 298.15 - 4.5756 \log(760/\rho). \quad (1)$$

In Eq. 1, $S^\circ(P, \alpha\text{-white}) = 9.82 \text{ gibbs/mol}^{-1}$,^{5a} $\Delta H_v^\circ = 14,080 \text{ cal mol}^{-1}$,^{7,10} and ρ , the vapor pressure of α -white phosphorus at 298.15°K , is equal to 0.0393 Torr.¹⁰ Thus,

$$S^\circ(P_4, g)_{298} = 66.89 \text{ gibbs mol}^{-1}.$$

The value calculated for $S^\circ(P_4, g)_{298}$ is also $66.89 \text{ gibbs mol}^{-1}$.

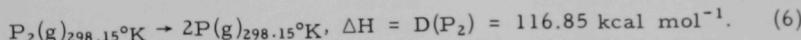
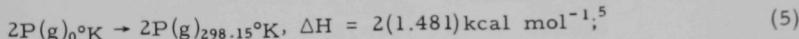
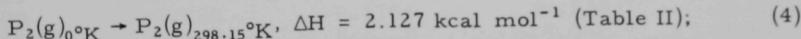
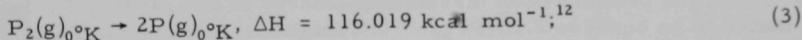
The enthalpy of formation of $P_4(g)$, which is the enthalpy of sublimation of α -white phosphorus, was reported by Dainton and Kimberley¹⁰ to be $14.04 \text{ kcal mol}^{-1}$; this value has recently been revised⁷ to $14.08 \text{ kcal mol}^{-1}$. Therefore, for the reaction



The thermodynamic data for $P_4(g)$ are in good agreement with the values given in a limited tabulation by Levine and Stull.¹¹

C. Monatomic Phosphorus, $P(g)$

The dissociation energy of $P_2(g)$ at 0°K , $D_0^\circ(P_2)$, is given by Herzberg¹² to be 5.031 eV ; enthalpy values for Reactions 3-5, when combined, yield a value for $\Delta H_f(P, g)$, as shown in Eq. 6.



Therefore, $\Delta H_f(P, g) = 58.43 \text{ kcal mol}^{-1}$.

D. Phosphorus Monofluoride, $PF(g)$

The spectroscopic constants reported by Douglas and Frackowiak (Table I and Ref. 13) have been used in the statistical calculations, and also to estimate a value for the dissociation energy of $PF(g)$.

A linear Birge-Sponer extrapolation yielded a value of 4.90 eV ($113.0 \text{ kcal mol}^{-1}$) for $D_{\text{LBS}}(PF)$; this value can be refined by using the following formula proposed by Hidenbrand:¹⁴

$$\frac{D(PF)}{D_{LBS}(PF)} = 0.365 \left(\frac{r_x}{r_e} \right) + 0.448. \quad (7)$$

In the above equation, $D(PF)$ is the refined dissociation energy, and r_x (in Å) can be calculated by means of

$$r_x = \frac{14.40}{IP(P) - EA(F)}, \quad (8)$$

where the symbols have the following significance: $IP(P)$ is the ionization potential of the phosphorus atom (10.49 eV),¹⁵ and $EA(F)$ is the electron affinity of fluorine (3.45 eV).¹⁶ From Eqs. 7 and 8 we derived

$$D(PF) = 4.49 \pm 0.25 \text{ eV} = 103.6 \pm 6 \text{ kcal mol}^{-1}.$$

The uncertainty has been estimated by comparison with analogous molecules. Since

$$\Delta Hf(PF, g) = \Delta Hf(P, g) + \Delta Hf(F, g) - D(PF), \quad (9)$$

$\Delta Hf(PF, g)$ is calculated to be $-26.3 \pm 6.0 \text{ kcal mol}^{-1}$. For the calculation of $\Delta Hf(PF, g)$, a value of $18.86 \text{ kcal mol}^{-1}$ was taken for $\Delta Hf(F, g)$.^{5b}

Thermodynamic data for PF are given in Table IV.

E. Phosphorus Difluoride, $PF_2(g)$

The primary bond dissociation energy in PF_3 , $D(PF_2-F)$, is estimated to be equal to $1.1\bar{D}(PF_3)$. This relationship holds for PCl_3 ^{17a} and $SbCl_3$.^{17b} Thus,

$$D(PF_2-F) \approx 1.1\bar{D}(PF_3) = 132.6 \pm 5 \text{ kcal mol}^{-1}. \quad (10)$$

For the reaction



Thus,

$$\Delta Hf^\circ(PF_2) = -115.7 \pm 5 \text{ kcal mol}^{-1}. \quad (12)$$

For the reaction



$\Delta Hf(PF_2, g)$ is calculated to be $-133 \pm 5 \text{ kcal mol}^{-1}$.

Thermodynamic data for PF_2 are given in Table V.

TABLE IV. Thermodynamic Properties of Phosphorus Monofluoride Gas

T (DEG.K.)	$-(G^{\circ} - H^{\circ})/T_0$ (GIBBS/MOL)	$(H^{\circ} - H^{\circ})/T_0$ (GIBBS/MOL)	S° (GIBBS/MOL)	Cp (GIBBS/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	39.001	6.9498	45.951	6.9568
200.00	43.824	6.9813	50.806	7.1301
273.15	46.011	7.0607	53.072	7.4357
298.15	46.631	7.0968	53.728	7.5456
300.00	46.675	7.0996	53.774	7.5536
400.00	48.739	7.2631	56.002	7.9355
500.00	50.378	7.4263	57.804	8.2060
600.00	51.745	7.5726	59.317	8.3899
700.00	52.922	7.6989	60.621	8.5163
800.00	53.957	7.8070	61.764	8.6054
900.00	54.882	7.8995	62.782	8.6701
1000.00	55.719	7.9790	63.698	8.7182
1100.00	56.482	8.0480	64.530	8.7548
1200.00	57.185	8.1081	65.293	8.7833
1300.00	57.836	8.1609	65.997	8.8058
1400.00	58.443	8.2077	66.651	8.8239
1500.00	59.011	8.2493	67.260	8.8387
1600.00	59.544	8.2865	67.831	8.8509
1700.00	60.048	8.3200	68.368	8.8610
1800.00	60.524	8.3503	68.874	8.8696
1900.00	60.976	8.3778	69.354	8.8769
2000.00	61.407	8.4029	69.810	8.8832
2200.00	62.210	8.4471	70.657	8.8933
2400.00	62.946	8.4846	71.431	8.9010
2600.00	63.627	8.5169	72.144	8.9070
2800.00	64.259	8.5449	72.804	8.9118
3000.00	64.849	8.5695	73.419	8.9157
3200.00	65.403	8.5913	73.994	8.9189
3400.00	65.925	8.6106	74.535	8.9216
3600.00	66.417	8.6280	75.045	8.9238
3800.00	66.884	8.6436	75.528	8.9257
4000.00	67.328	8.6577	75.986	8.9273
4200.00	67.751	8.6706	76.421	8.9287
4400.00	68.154	8.6823	76.837	8.9299
4600.00	68.540	8.6931	77.234	8.9309
4800.00	68.911	8.7031	77.614	8.9318
5000.00	69.266	8.7122	77.978	8.9327
5200.00	69.608	8.7207	78.329	8.9334
5400.00	69.937	8.7286	78.666	8.9340
5600.00	70.255	8.7360	78.991	8.9346
5800.00	70.562	8.7428	79.304	8.9351
6000.00	70.858	8.7492	79.607	8.9356

TABLE IV (Contd.)

T (DEG.K.)	$(H^\circ - H^\circ_{298})$ (KCAL/MOL)	$- \Delta H_f$ (KCAL/MOL)	$- \Delta G_f$ (KCAL/MOL)	LOG Kf
0.00	-2.1159	26.30	26.30	INF
100.00	-1.4209	26.30	26.64	58.23
200.00	-0.7196	26.30	26.99	29.49
273.15	-0.1873	26.30	27.26	21.81
298.15	0.0000	26.30	27.33	20.03
300.00	0.0140	26.30	27.34	19.91
400.00	0.7893	26.30	27.68	15.12
500.00	1.5973	26.31	28.03	12.25
600.00	2.4277	26.31	28.37	10.33
700.00	3.2733	26.32	28.71	8.96
800.00	4.1297	26.32	29.05	7.94
900.00	4.9936	26.33	29.40	7.14
1000.00	5.8631	26.34	29.74	6.50
1100.00	6.7369	26.35	30.07	5.98
1200.00	7.6138	26.36	30.41	5.54
1300.00	8.4933	26.38	30.75	5.17
1400.00	9.3748	26.39	31.08	4.85
1500.00	10.2580	26.40	31.42	4.58
1600.00	11.1425	26.42	31.75	4.34
1700.00	12.0281	26.44	32.09	4.12
1800.00	12.9146	26.46	32.42	3.94
1900.00	13.8020	26.47	32.75	3.77
2000.00	14.6900	26.49	33.08	3.61
2200.00	16.4677	26.54	33.73	3.35
2400.00	18.2471	26.58	34.39	3.13
2600.00	20.0280	26.64	35.03	2.94
2800.00	21.8099	26.69	35.68	2.78
3000.00	23.5927	26.75	36.32	2.65
3200.00	25.3761	26.82	36.95	2.52
3400.00	27.1602	26.89	37.59	2.42
3600.00	28.9447	26.96	38.21	2.32
3800.00	30.7297	27.03	38.83	2.23
4000.00	32.5150	27.12	39.45	2.16
4200.00	34.3006	27.20	40.07	2.09
4400.00	36.0864	27.29	40.68	2.02
4600.00	37.8725	27.38	41.29	1.96
4800.00	39.6588	27.48	41.89	1.91
5000.00	41.4452	27.58	42.49	1.86
5200.00	43.2318	27.69	43.08	1.81
5400.00	45.0186	27.80	43.67	1.77
5600.00	46.8054	27.91	44.26	1.73
5800.00	48.5924	28.03	44.84	1.69
6000.00	50.3795	28.15	45.42	1.65

TABLE V. Thermodynamic Properties of Phosphorus Difluoride Gas

T (DEG.K.)	$-(G^{\circ} - H_0^{\circ})/T$ (GIBBS/MOL)	$(H^{\circ} - H_0^{\circ})/T$ (GIBBS/MOL)	S° (GIBBS/MOL)	Cp° (GIBBS/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	44.523	7.9985	52.522	8.2203
200.00	50.174	8.4002	58.574	9.4388
273.15	52.851	8.8065	61.658	10.3805
298.15	53.629	8.9508	62.580	10.6721
300.00	53.684	8.9615	62.646	10.6928
400.00	56.340	9.5191	65.859	11.6328
500.00	58.518	10.0092	68.527	12.2628
600.00	60.381	10.4220	70.803	12.6812
700.00	62.014	10.7663	72.780	12.9655
800.00	63.471	11.0544	74.525	13.1648
900.00	64.787	11.2973	76.085	13.3087
1000.00	65.989	11.5040	77.493	13.4155
1100.00	67.094	11.6816	78.775	13.4967
1200.00	68.117	11.8356	79.952	13.5597
1300.00	69.069	11.9702	81.040	13.6095
1400.00	69.961	12.0888	82.050	13.6495
1500.00	70.799	12.1940	82.993	13.6821
1600.00	71.589	12.2878	83.877	13.7090
1700.00	72.336	12.3721	84.708	13.7314
1800.00	73.046	12.4482	85.494	13.7503
1900.00	73.721	12.5171	86.238	13.7664
2000.00	74.364	12.5799	86.944	13.7802
2200.00	75.569	12.6901	88.259	13.8024
2400.00	76.677	12.7835	89.460	13.8194
2600.00	77.703	12.8638	90.567	13.8327
2800.00	78.659	12.9334	91.593	13.8433
3000.00	79.554	12.9943	92.548	13.8518
3200.00	80.394	13.0481	93.442	13.8589
3400.00	81.187	13.0960	94.283	13.8647
3600.00	81.936	13.1388	95.075	13.8696
3800.00	82.648	13.1774	95.825	13.8737
4000.00	83.325	13.2123	96.537	13.8773
4200.00	83.970	13.2441	97.214	13.8803
4400.00	84.587	13.2730	97.860	13.8829
4600.00	85.177	13.2996	98.477	13.8853
4800.00	85.744	13.3241	99.068	13.8873
5000.00	86.288	13.3466	99.635	13.8891
5200.00	86.812	13.3675	100.180	13.8907
5400.00	87.317	13.3869	100.704	13.8921
5600.00	87.804	13.4050	101.209	13.8933
5800.00	88.275	13.4218	101.697	13.8945
6000.00	88.730	13.4376	102.168	13.8955

TABLE V (Contd.)

T (DEG.K.)	$(H^\circ - H_{298}^\circ)$ (KCAL/MOL)	$- \Delta H_f$ (KCAL/MOL)	$- \Delta G_f$ (KCAL/MOL)	LOG μ_e
0.00	-2.6687	132.50	132.50	INF
100.00	-1.8688	132.74	131.71	287.85
200.00	-0.9886	132.91	130.60	142.71
273.15	-0.2632	132.99	129.77	103.83
298.15	0.0000	133.00	129.45	94.89
300.00	0.0198	133.00	129.43	94.29
400.00	1.1390	133.05	128.23	70.06
500.00	2.3359	133.06	127.02	55.52
600.00	3.5845	133.07	125.81	45.83
700.00	4.8677	133.06	124.60	38.90
800.00	6.1748	133.05	123.39	33.71
900.00	7.4989	133.04	122.19	29.67
1000.00	8.8353	133.02	120.98	26.44
1100.00	10.1811	133.00	119.78	23.80
1200.00	11.5340	132.99	118.58	21.60
1300.00	12.8926	132.97	117.38	19.73
1400.00	14.2556	132.96	116.18	18.14
1500.00	15.6222	132.95	114.98	16.75
1600.00	16.9918	132.93	113.78	15.54
1700.00	18.3639	132.92	112.58	14.47
1800.00	19.7380	132.92	111.39	13.52
1900.00	21.1139	132.91	110.19	12.68
2000.00	22.4912	132.90	109.00	11.91
2200.00	25.2496	132.90	106.61	10.59
2400.00	28.0118	132.90	104.22	9.49
2600.00	30.7771	132.91	101.83	8.56
2800.00	33.5447	132.92	99.44	7.76
3000.00	36.3143	132.95	97.05	7.07
3200.00	39.0854	132.98	94.65	6.46
3400.00	41.8577	133.02	92.25	5.93
3600.00	44.6312	133.07	89.85	5.45
3800.00	47.4055	133.12	87.45	5.03
4000.00	50.1806	133.19	85.04	4.65
4200.00	52.9564	133.26	82.64	4.30
4400.00	55.7327	133.34	80.22	3.98
4600.00	58.5095	133.43	77.81	3.70
4800.00	61.2868	133.53	75.39	3.43
5000.00	64.0644	133.63	72.96	3.19
5200.00	66.8424	133.75	70.53	2.96
5400.00	69.6207	133.87	68.10	2.76
5600.00	72.3992	134.00	65.66	2.56
5800.00	75.1780	134.14	63.22	2.38
6000.00	77.9570	134.28	60.77	2.21

F. Phosphorus Trifluoride, PF₃(g)

Bond length and bond angle data for PF₃, based on an electron-diffraction study, have been determined by Hersch.¹⁸ Spectral data have been reported by several authors; the frequencies given by Levin and Abramowitz¹⁹ have been used in the calculations. The thermodynamic data for PF₃ (Table VI) are in reasonable agreement with other compilations.^{4,5,7}

A calorimetric study by Rudzitis, Van Deventer, and Hubbard²⁰ of the reaction



yielded a value of $-151.4 \pm 0.3 \text{ kcal mol}^{-1}$ for ΔH_r at 298.15°K. This value, when combined with $\Delta H_f(\text{PF}_5,\text{g}) = -398.05 \text{ kcal mol}^{-1}$ (Section H below), yields

$$\Delta H_f(\text{PF}_3,\text{g}) = -246.65 \pm 0.42 \text{ kcal mol}^{-1}.$$

G. Phosphorus Tetrafluoride, PF₄(g)

Estimated structural and spectral data for PF₄(g) (presented in Table VII) have been selected by analogy with the experimental values for PF₅(g). The geometrical configuration of PF₄, a transient species, was taken to be tetrahedral in accordance with the observations of Morton (e.p.r.)²¹ and Atkins and Symons (e.s.r.).²²

The enthalpy of formation of PF₄(g) was taken to be the mean, $-322 \pm 10 \text{ kcal mol}^{-1}$, of the enthalpies of formation of PF₃ and PF₅.

H. Phosphorus Pentafluoride, PF₅(g)

Two electron-diffraction investigations of PF₅, which yielded reasonably concordant results, have been reported by Hersch¹⁸ and by Hansen and Bartell.²³ The data from the latter investigation were used in the statistical calculations, along with the vibrational frequency assignments given by Hoskins and Lord.²⁴

The standard enthalpy of formation of PF₅(g) has been determined calorimetrically (O'Hare and Hubbard²⁵) by direct combination of α-white phosphorus and fluorine; the value reported, $-380.8 \pm 0.3 \text{ kcal mol}^{-1}$, was confirmed by Gross, Hayman, and Stuart,²⁶ who obtained $-381.4 \pm 0.8 \text{ kcal mol}^{-1}$. Therefore, for the reaction



$\Delta H_f(\text{PF}_5,\text{g})$ is calculated to be $-398.05 \pm 0.32 \text{ kcal mol}^{-1}$.

Table VIII lists the thermodynamic properties of PF₅(g).

TABLE VI. Thermodynamic Properties of Phosphorus Trifluoride Gas

T (DEG.K.)	$-(C-H_0^\circ)/T$ (GIBBS/MOL)	$(H^\circ-H_0^\circ)/T$ (GIBBS/MOL)	S (GIBBS/MOL)	C_p (GIBBS/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	44.967	8.1020	53.069	8.7405
200.00	50.868	9.1403	60.009	11.6203
273.15	53.853	10.0612	63.914	13.4789
298.15	54.748	10.3711	65.119	14.0272
300.00	54.812	10.3938	65.206	14.0659
400.00	57.963	11.5419	69.505	15.7912
500.00	60.646	12.5134	73.160	16.9279
600.00	63.001	13.3159	76.317	17.6782
700.00	65.105	13.9776	79.083	18.1867
800.00	67.009	14.5273	81.536	18.5427
900.00	68.747	14.9884	83.736	18.7995
1000.00	70.347	15.3795	85.727	18.9900
1100.00	71.829	15.7146	87.544	19.1347
1200.00	73.209	16.0045	89.214	19.2471
1300.00	74.500	16.2575	90.758	19.3358
1400.00	75.713	16.4800	92.193	19.4072
1500.00	76.857	16.6771	93.534	19.4653
1600.00	77.939	16.8529	94.792	19.5132
1700.00	78.966	17.0106	95.977	19.5532
1800.00	79.942	17.1529	97.095	19.5869
1900.00	80.873	17.2817	98.155	19.6155
2000.00	81.763	17.3991	99.162	19.6401
2200.00	83.431	17.6047	101.036	19.6797
2400.00	84.970	17.7789	102.749	19.7100
2600.00	86.400	17.9284	104.328	19.7337
2800.00	87.733	18.0580	105.791	19.7525
3000.00	88.983	18.1715	107.154	19.7678
3200.00	90.159	18.2717	108.431	19.7803
3400.00	91.269	18.3608	109.630	19.7906
3600.00	92.321	18.4404	110.762	19.7994
3800.00	93.320	18.5122	111.832	19.8067
4000.00	94.271	18.5771	112.848	19.8130
4200.00	95.179	18.6360	113.815	19.8185
4400.00	96.047	18.6899	114.737	19.8232
4600.00	96.879	18.7393	115.618	19.8273
4800.00	97.678	18.7847	116.462	19.8309
5000.00	98.445	18.8266	117.272	19.8341
5200.00	99.185	18.8654	118.050	19.8369
5400.00	99.897	18.9014	118.799	19.8394
5600.00	100.585	18.9350	119.520	19.8417
5800.00	101.250	18.9663	120.217	19.8437
6000.00	101.894	18.9955	120.889	19.8456

TABLE VI (Contd.)

T (DEG.K.)	$(H^\circ - H^\circ_{298})$ (KCAL/MOL)	- ΔH_f (KCAL/MOL)	- ΔG_f (KCAL/MOL)	LOG Kf
0.00	-3.0921	245.51	245.51	INF
100.00	-2.2819	246.09	243.08	531.26
200.00	-1.2641	246.48	239.90	262.15
273.15	-0.3439	246.63	237.52	190.04
298.15	0.0000	246.65	236.63	173.46
300.00	0.0260	246.65	236.57	172.34
400.00	1.5246	246.70	233.20	127.41
500.00	3.1646	246.68	229.83	100.46
600.00	4.8974	246.61	226.46	82.49
700.00	6.6922	246.52	223.11	69.66
800.00	8.5297	246.41	219.77	60.04
900.00	10.3975	246.29	216.45	52.56
1000.00	12.2874	246.17	213.14	46.58
1100.00	14.1939	246.04	209.84	41.69
1200.00	16.1133	245.90	206.56	37.62
1300.00	18.0426	245.77	203.28	34.17
1400.00	19.9799	245.63	200.02	31.22
1500.00	21.9236	245.50	196.76	28.67
1600.00	23.8726	245.37	193.52	26.43
1700.00	25.8259	245.23	190.28	24.46
1800.00	27.7830	245.10	187.06	22.71
1900.00	29.7432	244.97	183.83	21.15
2000.00	31.7060	244.85	180.62	19.74
2200.00	35.6381	244.60	174.21	17.31
2400.00	39.5772	244.36	167.82	15.28
2600.00	43.5217	244.13	161.45	13.57
2800.00	47.4704	243.91	155.10	12.11
3000.00	51.4225	243.71	148.77	10.84
3200.00	55.3773	243.51	142.44	9.73
3400.00	59.3344	243.32	136.13	8.75
3600.00	63.2935	243.15	129.83	7.88
3800.00	67.2541	242.99	123.54	7.10
4000.00	71.2161	242.84	117.26	6.41
4200.00	75.1792	242.71	110.98	5.77
4400.00	79.1434	242.58	104.71	5.20
4600.00	83.1085	242.47	98.45	4.68
4800.00	87.0743	242.37	92.19	4.20
5000.00	91.0408	242.28	85.93	3.76
5200.00	95.0079	242.20	79.67	3.35
5400.00	98.9756	242.14	73.43	2.97
5600.00	102.9437	242.09	67.18	2.62
5800.00	106.9122	242.04	60.93	2.30
6000.00	110.8812	242.02	54.69	1.99

TABLE VII. Thermodynamic Properties of Phosphorus Tetrafluoride Gas

T (DEG.K.)	-(G° H° ₀)/T (GIBBS/MOL)	(H°-H° ₀)/T (GIBBS/MOL)	S° (GIBBS/MOL)	C _P (GIBBS/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	45.601	7.9856	53.587	8.2319
200.00	51.340	8.8841	60.224	11.8047
273.15	54.282	10.0914	64.373	14.9055
298.15	55.185	10.5346	65.719	15.8356
300.00	55.250	10.5675	65.817	15.9013
400.00	58.530	12.2916	70.821	18.8304
500.00	61.440	13.8062	75.246	20.7635
600.00	64.073	15.0795	79.152	22.0444
700.00	66.480	16.1406	82.620	22.9162
800.00	68.694	17.0280	85.722	23.5284
900.00	70.744	17.7761	88.521	23.9713
1000.00	72.651	18.4129	91.064	24.3006
1100.00	74.432	18.9600	93.392	24.5512
1200.00	76.103	19.4344	95.537	24.7459
1300.00	77.675	19.8491	97.524	24.9000
1400.00	79.160	20.2145	99.374	25.0238
1500.00	80.566	20.5386	101.104	25.1248
1600.00	81.901	20.8279	102.729	25.2082
1700.00	83.171	21.0877	104.259	25.2778
1800.00	84.383	21.3221	105.706	25.3364
1900.00	85.542	21.5347	107.077	25.3863
2000.00	86.652	21.7284	108.380	25.4291
2200.00	88.739	22.0681	110.807	25.4982
2400.00	90.672	22.3563	113.028	25.5510
2600.00	92.471	22.6037	115.075	25.5923
2800.00	94.155	22.8184	116.973	25.6252
3000.00	95.735	23.0064	118.742	25.6518
3200.00	97.226	23.1724	120.398	25.6736
3400.00	98.635	23.3201	121.955	25.6917
3600.00	99.972	23.4523	123.424	25.7069
3800.00	101.243	23.5713	124.814	25.7198
4000.00	102.455	23.6790	126.134	25.7308
4200.00	103.612	23.7769	127.389	25.7403
4400.00	104.721	23.8664	128.587	25.7485
4600.00	105.783	23.9484	129.732	25.7557
4800.00	106.804	24.0238	130.828	25.7620
5000.00	107.786	24.0934	131.880	25.7675
5200.00	108.733	24.1579	132.891	25.7725
5400.00	109.645	24.2178	133.863	25.7769
5600.00	110.527	24.2736	134.801	25.7808
5800.00	111.380	24.3256	135.706	25.7844
6000.00	112.205	24.3743	136.580	25.7876

TABLE VII (Contd.)

T (DEG.K.)	$(H^\circ - H^\circ_{298})$ (KCAL/MOL)	- ΔH_f (KCAL/MOL)	- ΔG_f (KCAL/MOL)	LOG Kf
0.00	-3.1409	319.86	319.86	INF
100.00	-2.3423	320.80	315.80	690.19
200.00	-1.3641	321.57	310.48	339.28
273.15	-0.3844	321.93	306.43	245.17
298.15	0.0000	322.00	304.94	223.53
300.00	0.0294	322.01	304.83	222.07
400.00	1.7757	322.19	299.07	163.41
500.00	3.7622	322.23	293.29	128.20
600.00	5.9068	322.17	287.51	104.72
700.00	8.1575	322.04	281.74	87.96
800.00	10.4815	321.88	275.99	75.40
900.00	12.8576	321.69	270.27	65.63
1000.00	15.2720	321.48	264.56	57.82
1100.00	17.7151	321.26	258.88	51.44
1200.00	20.1803	321.03	253.22	46.12
1300.00	22.6629	320.80	247.58	41.62
1400.00	25.1593	320.56	241.96	37.77
1500.00	27.6669	320.31	236.35	34.44
1600.00	30.1837	320.07	230.76	31.52
1700.00	32.7081	319.82	225.19	28.95
1800.00	35.2389	319.58	219.63	26.67
1900.00	37.7751	319.34	214.08	24.63
2000.00	40.3159	319.09	208.55	22.79
2200.00	45.4090	318.62	197.52	19.62
2400.00	50.5141	318.15	186.53	16.99
2600.00	55.6286	317.69	175.58	14.76
2800.00	60.7505	317.25	164.67	12.85
3000.00	65.8783	316.82	153.78	11.20
3200.00	71.0109	316.40	142.93	9.76
3400.00	76.1475	315.99	132.10	8.49
3600.00	81.2874	315.60	121.29	7.36
3800.00	86.4301	315.23	110.50	6.36
4000.00	91.5751	314.87	99.74	5.45
4200.00	96.7223	314.53	88.99	4.63
4400.00	101.8712	314.20	78.26	3.89
4600.00	107.0216	313.89	67.54	3.21
4800.00	112.1734	313.59	56.83	2.59
5000.00	117.3263	313.31	46.14	2.02
5200.00	122.4803	313.05	35.46	1.49
5400.00	127.6353	312.80	24.80	1.00
5600.00	132.7911	312.57	14.13	0.55
5800.00	137.9476	312.35	3.47	0.13
6000.00	143.1048	312.15	-7.17	-0.26

TABLE VIII. Thermodynamic Properties of Phosphorus Pentafluoride Gas

T (DEG.K.)	$-(C^{\circ}-H_0^{\circ})/T$ (GIBBS/MOL)	$(H^{\circ}-H_0^{\circ})/T$ (GIBBS/MOL)	S° (GIBBS/MOL)	Cp° (GIBBS/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	46.839	8.2176	55.057	9.2552
200.00	53.025	10.0661	63.091	14.8313
273.15	56.429	11.8843	68.313	18.7436
298.15	57.496	12.5078	70.004	19.8796
300.00	57.574	12.5535	70.127	19.9594
400.00	61.511	14.8763	76.387	23.4841
500.00	65.049	16.8444	81.893	25.7870
600.00	68.268	18.4700	86.738	27.3078
700.00	71.220	19.8109	91.030	28.3413
800.00	73.940	20.9251	94.865	29.0666
900.00	76.460	21.8604	98.320	29.5912
1000.00	78.805	22.6539	101.459	29.9810
1100.00	80.997	23.3340	104.331	30.2776
1200.00	83.053	23.9227	106.976	30.5081
1300.00	84.989	24.4365	109.426	30.6904
1400.00	86.817	24.8886	111.705	30.8370
1500.00	88.548	25.2893	113.837	30.9565
1600.00	90.192	25.6467	115.838	31.0552
1700.00	91.756	25.9673	117.724	31.1375
1800.00	93.249	26.2565	119.505	31.2069
1900.00	94.676	26.5187	121.194	31.2660
2000.00	96.042	26.7573	122.799	31.3166
2200.00	98.612	27.1757	125.788	31.3983
2400.00	100.993	27.5303	128.523	31.4608
2600.00	103.209	27.8346	131.043	31.5097
2800.00	105.281	28.0986	133.380	31.5486
3000.00	107.228	28.3296	135.558	31.5801
3200.00	109.063	28.5336	137.596	31.6059
3400.00	110.798	28.7150	139.513	31.6273
3600.00	112.444	28.8773	141.322	31.6453
3800.00	114.010	29.0234	143.033	31.6605
4000.00	115.502	29.1556	144.657	31.6735
4200.00	116.927	29.2758	146.203	31.6847
4400.00	118.292	29.3855	147.677	31.6945
4600.00	119.600	29.4861	149.086	31.7030
4800.00	120.857	29.5786	150.436	31.7104
5000.00	122.066	29.6640	151.730	31.7170
5200.00	123.231	29.7431	152.974	31.7229
5400.00	124.355	29.8165	154.172	31.7281
5600.00	125.441	29.8849	155.326	31.7327
5800.00	126.491	29.9487	156.439	31.7369
6000.00	127.507	30.0083	157.515	31.7407

TABLE VIII (Contd.)

T (DEG.K.)	$(H^\circ - H_{298}^\circ)$ (KCAL/MOL)	$- \Delta H_f$ (KCAL/MOL)	$- \Delta G_f$ (KCAL/MOL)	LOG Kf
0.00	-3.7292	395.44	395.44	INF
100.00	-2.9075	396.70	389.82	851.96
200.00	-1.7160	397.61	382.55	418.03
273.15	-0.4830	397.98	377.04	301.68
298.15	0.0000	398.05	375.04	274.91
300.00	0.0369	398.06	374.90	273.12
400.00	2.2213	398.19	367.16	200.60
500.00	4.6930	398.14	359.40	157.09
600.00	7.3528	397.98	351.67	128.09
700.00	10.1384	397.75	343.96	107.39
800.00	13.0109	397.47	336.30	91.87
900.00	15.9451	397.16	328.67	79.81
1000.00	18.9246	396.83	321.08	70.17
1100.00	21.9382	396.49	313.52	62.29
1200.00	24.9780	396.13	306.00	55.73
1300.00	28.0382	395.77	298.50	50.18
1400.00	31.1149	395.40	291.03	45.43
1500.00	34.2048	395.03	283.59	41.32
1600.00	37.3055	394.66	276.17	37.72
1700.00	40.4153	394.29	268.77	34.55
1800.00	43.5326	393.92	261.41	31.74
1900.00	46.6563	393.55	254.05	29.22
2000.00	49.7855	393.18	246.72	26.96
2200.00	56.0574	392.46	232.11	23.06
2400.00	62.3435	391.74	217.56	19.81
2600.00	68.6408	391.05	203.08	17.07
2800.00	74.9468	390.36	188.64	14.72
3000.00	81.2597	389.70	174.26	12.69
3200.00	87.5784	389.05	159.92	10.92
3400.00	93.9018	388.42	145.62	9.36
3600.00	100.2291	387.81	131.35	7.97
3800.00	106.5597	387.21	117.11	6.74
4000.00	112.8931	386.64	102.91	5.62
4200.00	119.2290	386.09	88.74	4.62
4400.00	125.5669	385.55	74.60	3.71
4600.00	131.9067	385.04	60.48	2.87
4800.00	138.2481	384.54	46.37	2.11
5000.00	144.5908	384.07	32.29	1.41
5200.00	150.9348	383.61	18.23	0.77
5400.00	157.2799	383.18	4.19	0.17
5600.00	163.6260	382.76	-9.85	-0.38
5800.00	169.9730	382.37	-23.86	-0.90
6000.00	176.3208	381.99	-37.86	-1.38

I. Tetrafluorodiphosphine, $P_2F_4(g)$

Rudolph, Taylor, and Parry²⁷ described the synthesis of P_2F_4 and reported values for 10 fundamental vibrational frequencies. The other fundamentals, at 204 and 150 cm^{-1} , have been estimated by analogy with P_2Cl_4 .²⁸ The estimates of the bond lengths and bond angles (Table I) are based on published structural data for P_2I_4 ²⁹ and P_2H_4 ;³⁰ P_2F_4 was assumed to have a trans structure.²⁷

The enthalpy of formation of P_2F_4 can be calculated from the equation

$$\Delta H_f(P_2F_4, g) = 2\Delta H_f(PF_2, g) - D(F_2P-PF_2). \quad (16)$$

Since no experimental data are available for $D(F_2P-PF_2)$, this quantity has had to be estimated. The principal considerations on which the estimate has been based are as follows:

1. The P-P bond in P_2F_4 is stronger than the N-N bond (22 kcal mol^{-1})^{5c} in N_2F_4 .³¹

2. The P-P stretching force-constant is larger in P_2F_4 ²⁷ than in P_2Cl_4 .²⁸ Consequently, $D(F_2P-PF_2)$ will probably be larger than $D(Cl_2P-PCl_2)$.

3. $D(Cl_2P-PCl_2)$ has been recalculated from the appearance potential measurements of Sandoval, Moser, and Kiser.³² The value so obtained, 63 ± 5 kcal mol^{-1} , is based on a more recent value, 84 kcal mol^{-1} ,^{17a} for $D(PCl_2-Cl)$.

4. Theoretical arguments³³ suggest that the P-P bond strength is greater in P_2F_4 than in P_2Cl_4 .

Thus, $D(F_2P-PF_2)$ has been estimated to be 68 ± 10 kcal mol^{-1} , and, from Eq. 16, $\Delta H_f(P_2F_4, g)$ has been calculated to be -334 ± 15 kcal mol^{-1} . The thermodynamic properties of P_2F_4 are given in Table IX.

IV. SOME OBSERVATIONS ON THE THERMODYNAMICS OF THE PHOSPHORUS-FLUORINE SYSTEM

Some of the thermodynamic data given in this report have been used to calculate ΔG° and log K values at various temperatures (see Tables X-XII) for the following decomposition reactions:

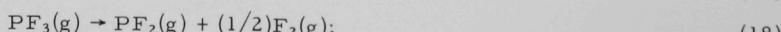


TABLE IX. Thermodynamic Properties of Tetrafluorodiphosphine Gas

T (DEG.K.)	$-(C-H_0^\circ)/T$ (GIBBS/MOL)	$(H^\circ-H_0^\circ)/T$ (GIBBS/MOL)	δ (GIBBS/MOL)	G° (GIBBS/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	51.500	9.3177	60.818	12.3166
200.00	58.935	12.5139	71.449	18.7560
273.15	63.161	14.6639	77.825	22.1534
298.15	64.474	15.3317	79.806	23.0850
300.00	64.569	15.3797	79.949	23.1497
400.00	69.323	17.6957	87.019	25.9165
500.00	73.477	19.5249	93.002	27.6333
600.00	77.170	20.9741	98.144	28.7293
700.00	80.493	22.1374	102.631	29.4573
800.00	83.513	23.0856	106.599	29.9602
900.00	86.279	23.8705	110.150	30.3199
1000.00	88.829	24.5293	113.359	30.5851
1100.00	91.194	25.0894	116.283	30.7856
1200.00	93.398	25.5708	118.969	30.9407
1300.00	95.462	25.9887	121.451	31.0629
1400.00	97.402	26.3548	123.756	31.1609
1500.00	99.231	26.6780	125.909	31.2406
1600.00	100.962	26.9652	127.927	31.3062
1700.00	102.605	27.2222	129.827	31.3609
1800.00	104.167	27.4535	131.621	31.4070
1900.00	105.658	27.6626	133.320	31.4461
2000.00	107.081	27.8527	134.934	31.4796
2200.00	109.752	28.1849	137.937	31.5337
2400.00	112.217	28.4658	140.683	31.5750
2600.00	114.505	28.7063	143.211	31.6072
2800.00	116.640	28.9144	145.555	31.6328
3000.00	118.641	29.0964	147.738	31.6536
3200.00	120.524	29.2567	149.781	31.6706
3400.00	122.302	29.3992	151.702	31.6847
3600.00	123.987	29.5265	153.513	31.6965
3800.00	125.586	29.6409	155.227	31.7065
4000.00	127.109	29.7444	156.854	31.7151
4200.00	128.563	29.8385	158.401	31.7225
4400.00	129.953	29.9243	159.877	31.7289
4600.00	131.285	30.0028	161.288	31.7345
4800.00	132.563	30.0751	162.638	31.7394
5000.00	133.792	30.1418	163.934	31.7437
5200.00	134.976	30.2034	165.179	31.7475
5400.00	136.117	30.2607	166.377	31.7510
5600.00	137.218	30.3140	167.532	31.7540
5800.00	138.283	30.3637	168.646	31.7568
6000.00	139.313	30.4102	169.723	31.7593

TABLE IX (Contd.)

T (DEG.K.)	$(H^o - H^o_{298})$ (KCAL/MOL)	- ΔHf (KCAL/MOL)	- ΔGf (KCAL/MOL)	LOG Kf
0.00	-4.5711	332.22	332.22	INF
100.00	-3.6394	333.38	326.89	714.42
200.00	-2.0684	333.91	320.15	349.85
273.15	-0.5657	334.01	315.16	252.16
298.15	0.0000	334.00	313.37	229.71
300.00	0.0428	334.00	313.24	228.20
400.00	2.5072	333.86	306.34	167.38
500.00	5.1913	333.61	299.49	130.91
600.00	8.0133	333.29	292.70	106.61
700.00	10.9250	332.93	285.96	89.28
800.00	13.8973	332.55	279.28	76.29
900.00	16.9123	332.16	272.64	66.21
1000.00	19.9582	331.75	266.05	58.15
1100.00	23.0272	331.34	259.50	51.56
1200.00	26.1138	330.93	252.99	46.07
1300.00	29.2142	330.52	246.51	41.44
1400.00	32.3256	330.10	240.06	37.47
1500.00	35.4458	329.69	233.64	34.04
1600.00	38.5732	329.28	227.25	31.04
1700.00	41.7067	328.87	220.89	28.40
1800.00	44.8451	328.46	214.55	26.05
1900.00	47.9878	328.05	208.23	23.95
2000.00	51.1342	327.65	201.93	22.07
2200.00	57.4357	326.85	189.40	18.82
2400.00	63.7468	326.07	176.94	16.11
2600.00	70.0651	325.30	164.54	13.83
2800.00	76.3892	324.54	152.21	11.88
3000.00	82.7179	323.81	139.93	10.19
3200.00	89.0504	323.08	127.69	8.72
3400.00	95.3860	322.37	115.50	7.42
3600.00	101.7241	321.67	103.35	6.27
3800.00	108.0645	320.99	91.24	5.25
4000.00	114.4066	320.33	79.16	4.33
4200.00	120.7504	319.69	67.12	3.49
4400.00	127.0956	319.06	55.11	2.74
4600.00	133.4419	318.44	43.13	2.05
4800.00	139.7893	317.84	31.17	1.42
5000.00	146.1376	317.26	19.23	0.84
5200.00	152.4867	316.69	7.32	0.31
5400.00	158.8366	316.14	-4.56	-0.18
5600.00	165.1871	315.61	-16.43	-0.64
5800.00	171.5382	315.09	-28.28	-1.07
6000.00	177.8898	314.59	-40.11	-1.46

TABLE X. Thermodynamic Data for the Reaction $\text{PF}_5(\text{g}) \rightarrow \text{PF}_3(\text{g}) + \text{F}_2(\text{g})$

T (°K)	298.15	400	600	800	1000	1200	1400	1600	1800	2000
$\Delta G^\circ (\text{kcal mol}^{-1})$	138.4	134.0	125.2	116.5	107.9	99.4	91.0	82.7	74.4	66.1
log Kf	-101	-73	-46	-32	-24	-18	-14	-11	-9	-7

TABLE XI. Thermodynamic Data for the Reaction $\text{PF}_3(\text{g}) \rightarrow \text{PF}_2(\text{g}) + (1/2)\text{F}_2(\text{g})$

T (°K)	298.15	400	600	800	1000	1200	1400	1600	1800	2000
$\Delta G^\circ (\text{kcal mol}^{-1})$	107.2	105.0	100.7	96.4	92.2	88.0	83.8	79.7	75.7	71.6
log Kf	-79	-57	-37	-26	-20	-16	-13	-11	-9	-8

TABLE XII. Thermodynamic Data for the Reaction $\text{P}_2\text{F}_4(\text{g}) \rightarrow 2\text{PF}_2(\text{g})$

T (°K)	298.15	400	600	800	1000	1200	1400	1600	1800	2000
$\Delta G^\circ (\text{kcal mole}^{-1})$	54.5	49.9	41.1	32.5	24.1	15.8	7.7	-0.3	-8.2	-16.1
log Kf	-40	-27	-15	-9	-5	-3	-1	0	1	2

Extending the calculations to higher temperatures indicates that decomposition of PF_5 according to Eq. 17 probably does not become significant until the temperature reaches approximately 3500°K. At that temperature, the mole fraction of fluorine in the equilibrium mixture is approximately 0.03. It is obvious that PF_5 has greater thermal stability than AsF_5 .^{1b}

The data in Table XII indicate that P_2F_4 is stable at relatively high temperatures. However, the ΔG_f values for the decomposition of P_2F_4 are uncertain by about ± 20 kcal/mol⁻¹. Thus, for example, the value for Kf at 1000°C is uncertain by almost 100%.

ACKNOWLEDGMENT

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